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PROPERTIES OF COATINGS OBTAINED IN TREATMENT OF SILICATE GLASSES IN POTASSIUM AND LEAD NITRATE MELTS¹

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The effect of the duration of treatment of the surface of soda-lime glass in potassium and lead nitrate melts at a temperature of 460°C on the chemical and mechanical strength is investigated. It is demonstrated that the formation of a crystalline lead-silicate coating in this treatment increases the alkali resistance threefold and the mechanical strength of glass twofold. Practical recommendations are issued.

Formation of various coatings on the surface of soda-lime glasses significantly expands their application areas, since it makes it possible to improve various service properties and/or impart new characteristics to products (functional coatings).

Treatment of soda-lime glasses in nitrate melts is a well-known method of modification of the composition and properties of surface layers (strengthening, control of optical characteristics, etc.) [1].

The presence of bivalent ions (R^{2+}) in a salt melt is undesirable for ion-exchange processes, since it decreases the effect of treatment by blocking ion-exchange surface centers [2, 3]. However, it is demonstrated in some publications that with a sufficiently high content of bivalent metal nitrates, crystalline coatings are formed on the surface of silicate glasses, for instance $2BaO \cdot 3SiO_2$ coating after treatment in KNO_3 melts with a molar content over 5% barium nitrate or $4PbO \cdot SiO_2 - PbO$ after treatment in KNO_3 melts containing over 3% lead nitrate [4, 5].

Consequently, the formation of crystalline coatings on the surface of silicate glasses treated in melted salts of the system $KNO_3 - R(NO_3)_2$ can be considered as an alternative method for the formation of thick film coatings for various purposes. Thus, coatings based on PbO are used in electronics as promoters of adhesion of PZT films to various substrates [6]. To identify other areas of possible application, it is necessary to study the effect of treatment on the properties of substrate.

The present study investigates the structure and properties of coatings obtained in the treatment of soda-lime glass in a melt with a mass content of 90% KNO_3 and 10% $Pb(NO_3)_2$. The substrate was vertically drawn sheet glass

(nominal thickness 4 mm) of the following chemical composition (wt.%): 72.9 SiO_2 , 1.5 Al_2O_3 , 9.6 CaO , 2.4 MgO , 13.2 Na_2O , 0.1 K_2O , 0.2 SO_3 , and 0.1 Fe_2O_3 .

Based on the previous studies [5], a temperature of 460°C was chosen as optimum, since it ensures stability of the lead content in salt melts in treatment.

The structure and composition of the resulting coatings was studied using a Jeol 6300 electron microscope equipped with a EDS-S60 DX90 x-ray microanalyzer, a Philips X'Pert-MPD diffractometer, and a Nicolet AVATAR 320 FT-IR microscope.

The mechanical strength was determined by the central symmetric bending method and the chemical resistance was measured by the powder method according to GOST 10134-62 (glass powder of the same chemical composition treated in salt melt was used for testing).

The concentration variation of the main components of the coating (PbO) and glass (SiO_2) in the surface layers, as the treatment duration increases, is shown in Fig. 1. The chemical composition of the coating is a relatively constant

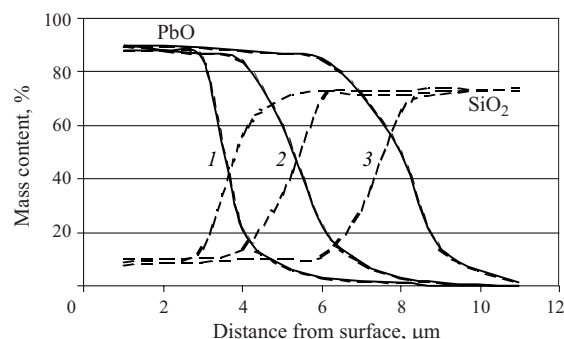


Fig. 1. Distribution of main components over surface layers of lead-silicate coating. Treatment at 460°C for 0.5 (1), 1.0 (2), and 1.5 h (3).

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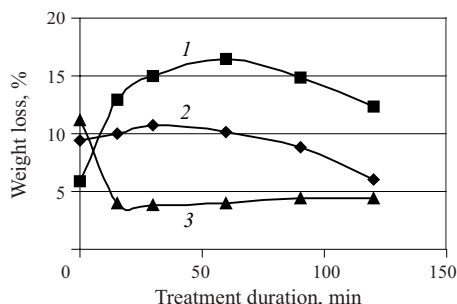


Fig. 2. Chemical resistance of glass depending on duration of treatment in salt melts: 1, 2, and 3) acid, water, and alkali resistance, respectively.

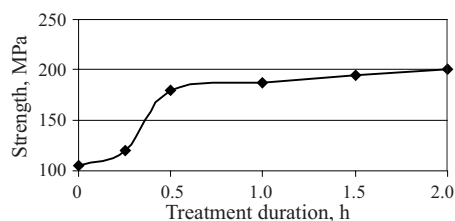


Fig. 3. The effect of treatment duration on mechanical strength of glass.

value, which points to the formation of a new lead-silicate crystalline phase of the following approximate composition (mol. %): 66 PbO, 29 PbO, and 5 CaO. Identification of the phase composition of the coating is difficult, as the diffraction pattern peaks differ somewhat in the values of angle 2θ and intensity from the standard data; however, they are close to a combination of peaks PbO, Pb_2O_3 , PbO_2 , $3\text{PbO} \cdot 2\text{SiO}_2$, and $4\text{PbO} \cdot \text{SiO}_2$.

The effect of the coating on the chemical resistance of glass is indicated in Fig. 2. Considering the higher basicity of the chemical composition of the coating, it is easy to account for the increased alkali resistance (approximately 3 times) and decreased alkali resistance (approximately 3 times as well). Water resistance in short-term treatment somewhat decreases; however, it grows with increasing thickness of the coating, which can be attributed to impeded diffusion of alkali ions from the glass via the coating and the formation of a more cohesive surface layer structure.

Thus, formation of a lead-silicate coating on the surface of soda-lime glass can be recommended for treatment of glass articles that operate in contact with aggressive alkali media (for instance, treatment of the surface of laboratory glassware or glass pipelines and mixing reactors at chemical plants). It is also advisable to use soda-lime glass fiber treated in a $\text{KNO}_3 - \text{Pb}(\text{NO}_3)_2$ melt to reinforce cement stone. A short-term (15 min) thermochemical treatment significantly increases the alkali resistance of the glass surface and can prevent its corrosion in a curing cement melt [7].

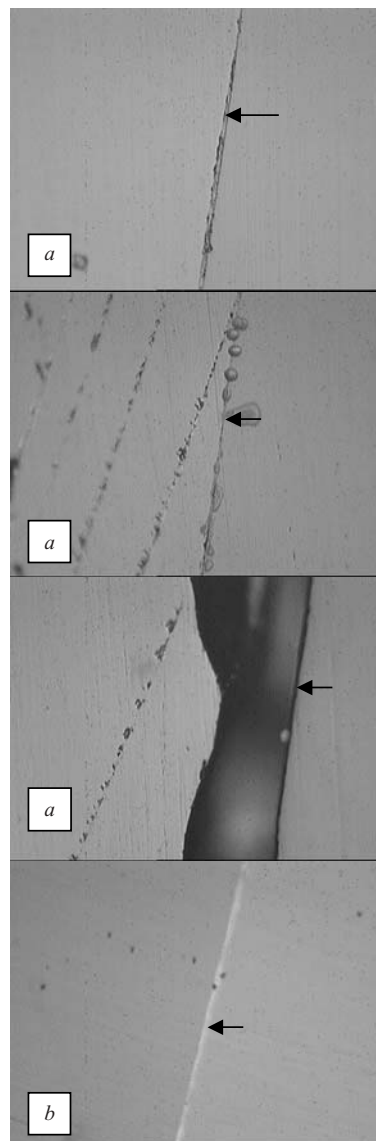


Fig. 4. Microphotos ($\times 200$) of seals between soda-lime (to the right of the seal boundary) and lead-silicate (to the left of the seal boundary) glasses obtained without (a) and with (b) a coating. The arrow indicates the seal boundary.

The effect of treatment in a melt of the $\text{KNO}_3 - \text{Pb}(\text{NO}_3)_2$ system on the mechanical strength of sheet glass is shown in Fig. 3. Treatment for 0.5 – 1.0 h makes it possible to raise the mechanical strength of glass 1.8 – 2.0 times. The presence of an induction period (about 0.3 h) points to the necessity of initial structural modification in the surface glass layers, before the formation of a lead-silicate crystalline coating. Considering that a high concentration of lead ions in a melt delays the ion-exchange processes of K^+ (melt) \leftrightarrow Na^+ (glass), and the depth of penetration of K^+ ions into glass does not exceed 2 μm , it can be assumed that the strengthening effect is due not so much to ion exchange as to the formation of a crystalline coating that is structurally related to the substrate. Thus, an increase in me-

chanical strength is another argument in favor of using this method for treatment of soda-lime glass fiber used as reinforcement in the production of glass-cement composites.

Another promising use of the proposed method is in the production of glass seals of $\text{Na}_2\text{O} - \text{CaO} - \text{SiO}_2$ system glasses with lead silicate glasses. Sealing soda-lime glass (both initial and treated for 1 h in $\text{KNO}_3 - \text{Pb}(\text{NO}_3)_2$ at 460°C) to lead silicate glass of the composition (wt.%) 55.3 SiO_2 , 29.7 PbO , 2.0 Al_2O_3 , 3.8 Na_2O , and 9.2 K_2O was carried out at a temperature of 620°C . Microphotos of the obtained seals are shown in Fig. 4. The presence on treated glass surface of a transitional layer about $10\text{ }\mu\text{m}$ thick that has a concentration gradient of PbO and SiO provides for the coordination of TCLEs of sealed glasses and the formation of a homogenous seal structure and prevents formation of defects in the form of flaking, microbubbles, and large bubbles, which are present in a seal of nontreated glasses.

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